

Topics in Shale Gas



**Quality Systems for Hydrocarbon Analyses:
Similarities and Differences between EPA, ASTM and
GPA methods – Considerations for a more Unified
Approach**

August 9, 2016 NEMC Anaheim, California

**Rock J. Vitale, CEAC
Michael R. Green, Ph.D.
David A. Gratson, CEAC
Environmental Standards Inc.**

W. James Bover, Ph.D., WJB Consulting LLC

J. Andrew Tachovsky, P.E., Sabine River Partners

Agenda

1 Current Issues Impacting Oil/Gas Analysis

2 Elements of Quality System

3 Overview of EPA, ASTM, GPA Methods

4 Unification

Recent Developments in Hydrocarbon Testing

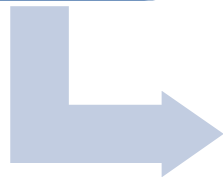
**Tier III Vehicle
Emission and Fuel
Standards - 40 CFR
Part 80, Subpart D**

Change from
prescriptive ASTM
test method to
§80.47:
Performance-based
Analytical Test
Method

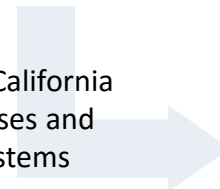
Tier III Revisions:
Testing of
reformulated
gasoline. As of
January 2016
require sampling
and subsequent
analysis per §80.47

Flash Gas Emission Estimates (e.g. Section 114 “request” of E&P operators)

Analysis of
pressurized
sample
(condensate, oil,
water) e.g. CARB
Appendix B*



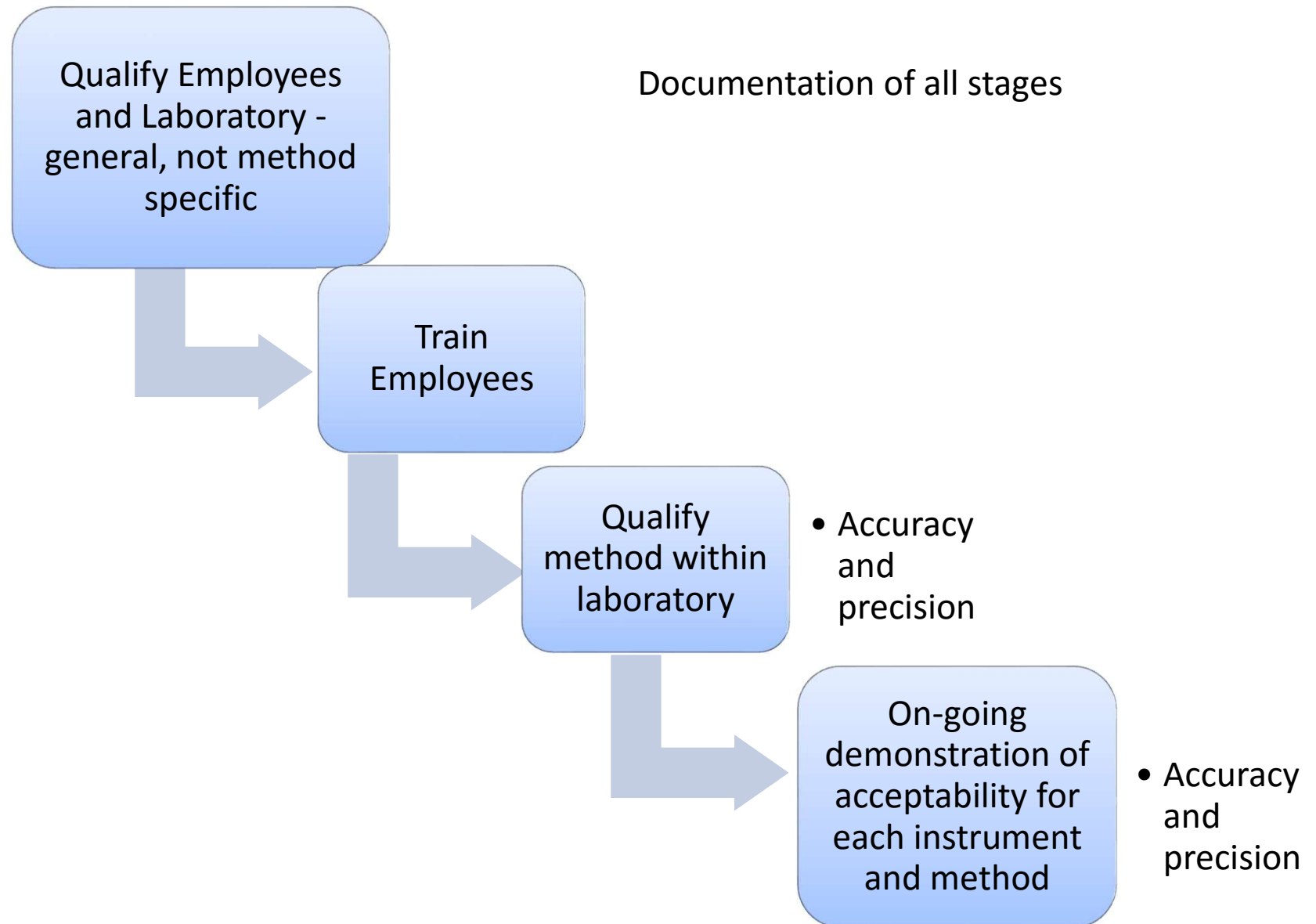
Methods include
ASTM (e.g. D2597);
GPA (e.g. 2177,
2286); and U S EPA
(e.g. Method TO-
15, 8260)



EPA, ASTM,
and GPA all
have separate
QC Practices

*Regulation for the Mandatory Reporting of Greenhouse Gas Emissions , California
Air Resources Board 2013 Appendix B: Flash Emissions of Greenhouse Gases and
Other Compounds from Crude Oil and Natural Gas Separator and Tank Systems

Elements of a Quality System



Quality System Terms

EPA: Blank, LFB/LCS, Duplicates, Matrix Spikes, PE Sample, Surrogates, Internal Standards

GPA: Repeatability, Reproducibility, Reference standard blend, Linearity Plot, Fidelity Plots

ASTM: Repeatability, Reproducibility, SQC, check standard, internal standards, proficiency test samples, verification samples, CRM

Shall/Should/Recommend

Incorporation by Reference

GPA Quality Practices

Fidelity of Reference Standards
(initial and on-going comparison with historic known standards)

Determination of Linear Range
(includes linearity review)

**As stated in GPA
Methods 2198, 2261**

Control Charts (20 separate days, establish limits, outlier tests)

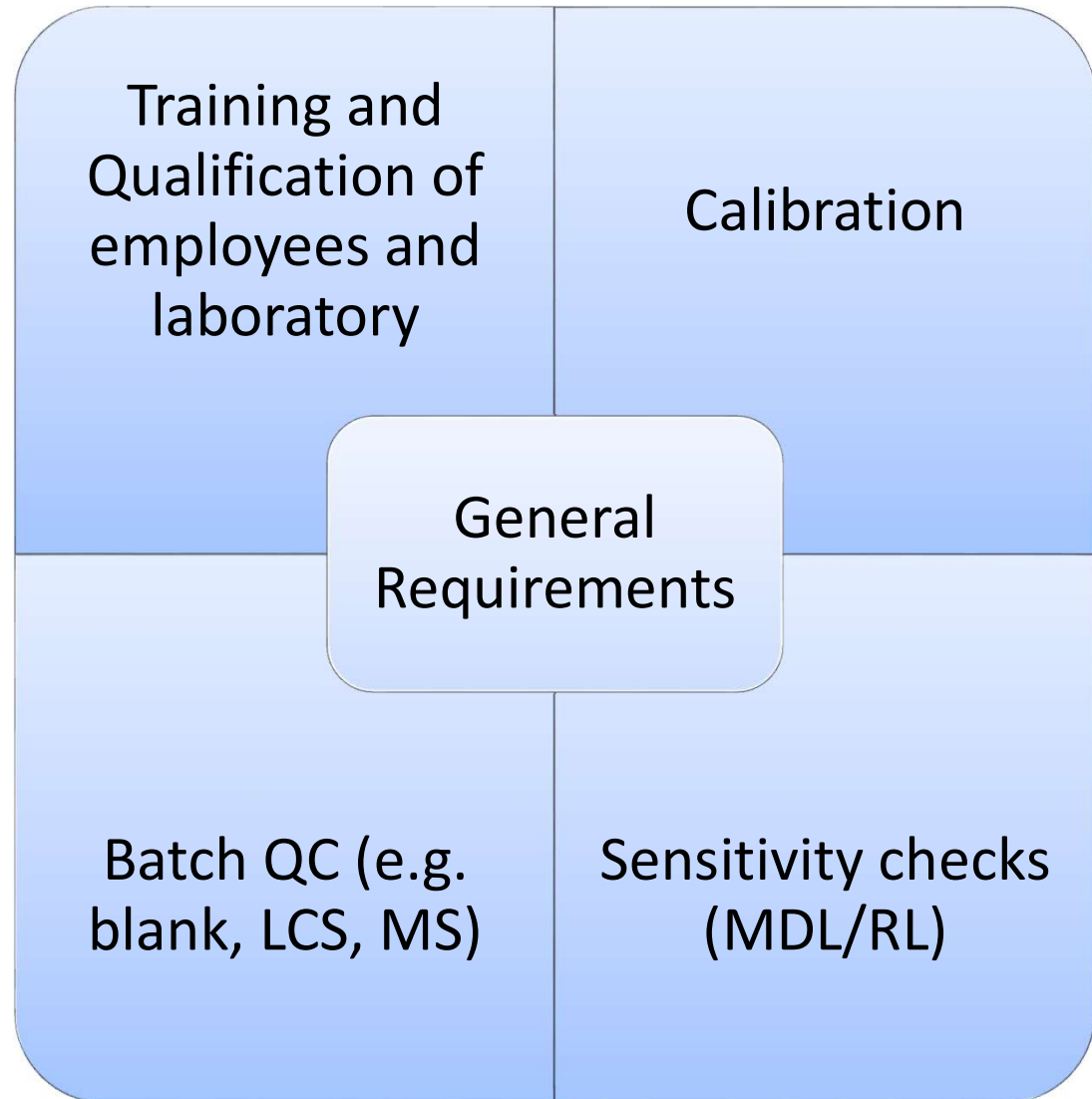
Calibration (single and multi-point, certified standard, verify repeatability, monitor regularly)

US EPA Quality Practices

Method (Program)
specific QC

Proficiency Testing
required with some
programs & state
accreditation

RCRA includes
performance-based
allowances



US EPA Quality Practices

Consider Methods 8260 and
TO-15 (cited by CARB) continued

- Demonstration of Method Capability
 - TO-15 has sensitivity, precision, and accuracy limits - method defined.
 - 8260 has generic starting limits, with recommendation for in-house derivation. Not based on inter-laboratory studies.
- Initial Calibration (linearity/sensitivity)

US EPA Quality Practices

Consider Methods 8260 and
TO-15 (cited by CARB)

- **Batch Quality Control**
 - Daily calibration
 - Blank (negative control)
 - Internal Standards/Surrogates
 - Sensitivity (MDL, RL)
 - Precision (duplicates) & Accuracy (check stds) assessment
- Qualitative Criteria
- Method Performance Information (no required use)
 - Single and multi-laboratory precision and accuracy

The NELAC Institute

Environmental Laboratory Sector - Technical Requirements (2009)

- Quantification formulae
- Qualitative/selectivity
- Constant/reproducible test conditions
- Reagents and standards quality
- Calibration
- Measurement traceability
- Batch Quality Control
 - Positive & negative control
 - Precision
 - Accuracy
 - Sensitivity (RL, MDL)
- **PT Studies for Accreditation**

ASTM Quality Practices – D2

D6792 QA System– Technical Requirements

- Calibration (test method specific) & Verification (CRM)
- Quality Control Practices
 - Control charts, per D6299
 - Accuracy, precision
 - “Regular” analysis of QC samples (9%, then per TPI & PT results)
 - QC expressed as both repeatability & reproducibility
 - QC sample: stable/homogeneous/similar to samples.

ASTM Quality Practices – D2

D6792 QA System– Technical Requirements

- Repeatability: single operator, instrument, back to back
- Reproducibility: between laboratories (personnel + instruments)
- Test Performance Index (TPI): compare laboratory precision with published reproducibility
 - $TPI = \frac{\text{Test Method reproducibility}}{\text{site precision}}$ Lab precision should be better than inter-laboratory reproducibility

ASTM Quality Practices System – D2

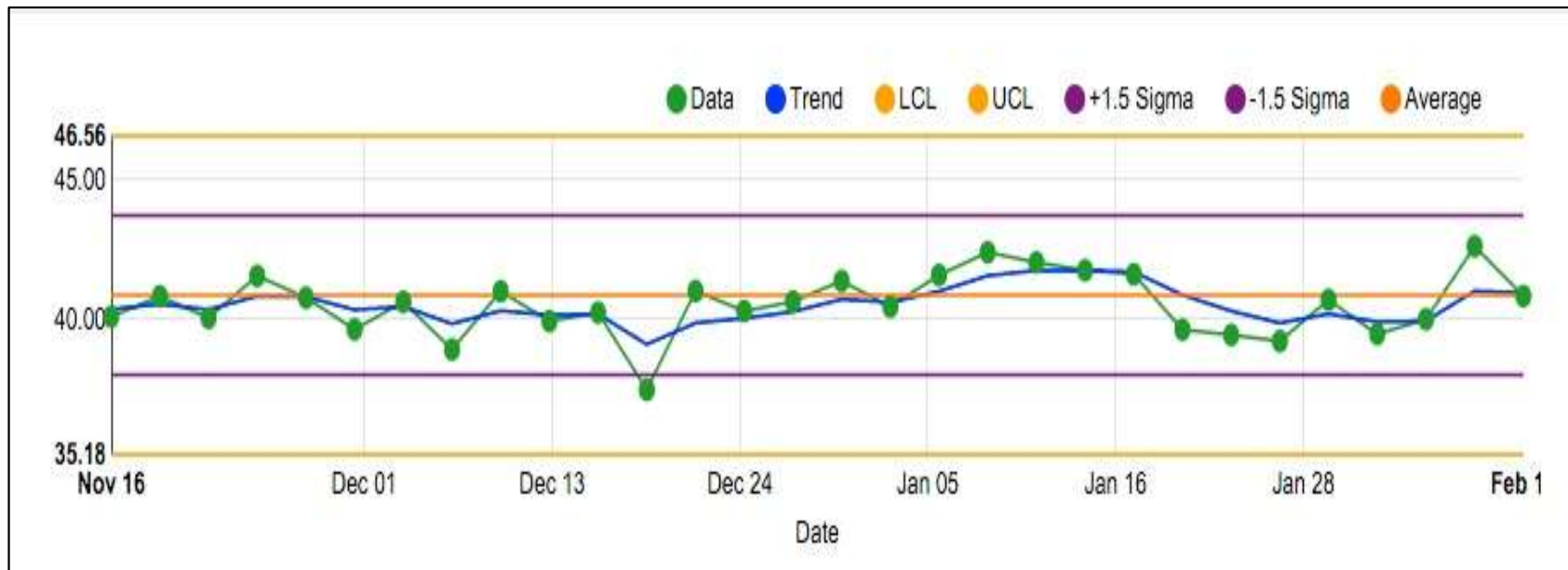
D6299 Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

- Provides practices for quality control and control charting
 - Reference Material Analysis
 - Stability and Precision QC Testing
 - Accuracy Monitoring
 - Charting Proficiency Testing Data
 - Periodic, Independent System Validation (Validation Audit)

Note, there are ASTM standards for general practices included in E260 and E355 (gas chromatography).

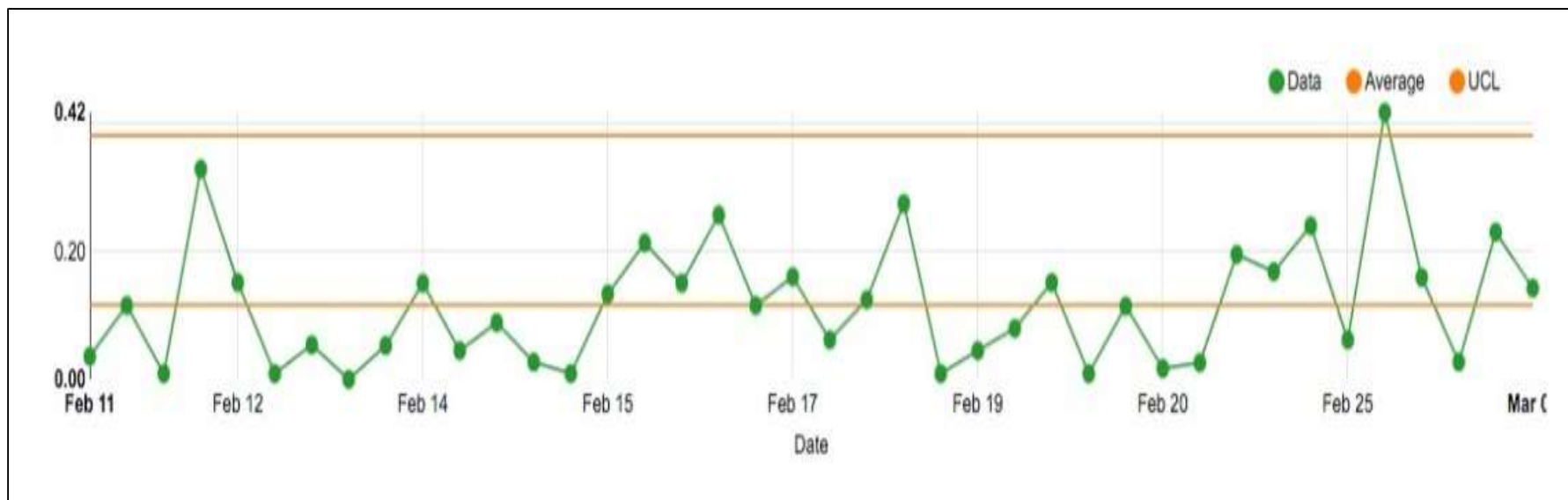
ASTM D6299 and 40 CFR 80.47

- ASTM D6299 was incorporated by reference into 40 CFR 80.47. As such, compliance with both ASTM D6299 and 40 CFR 80.47 may expect to generate the same statistical evaluations:
- I charts
- Outlier evaluation

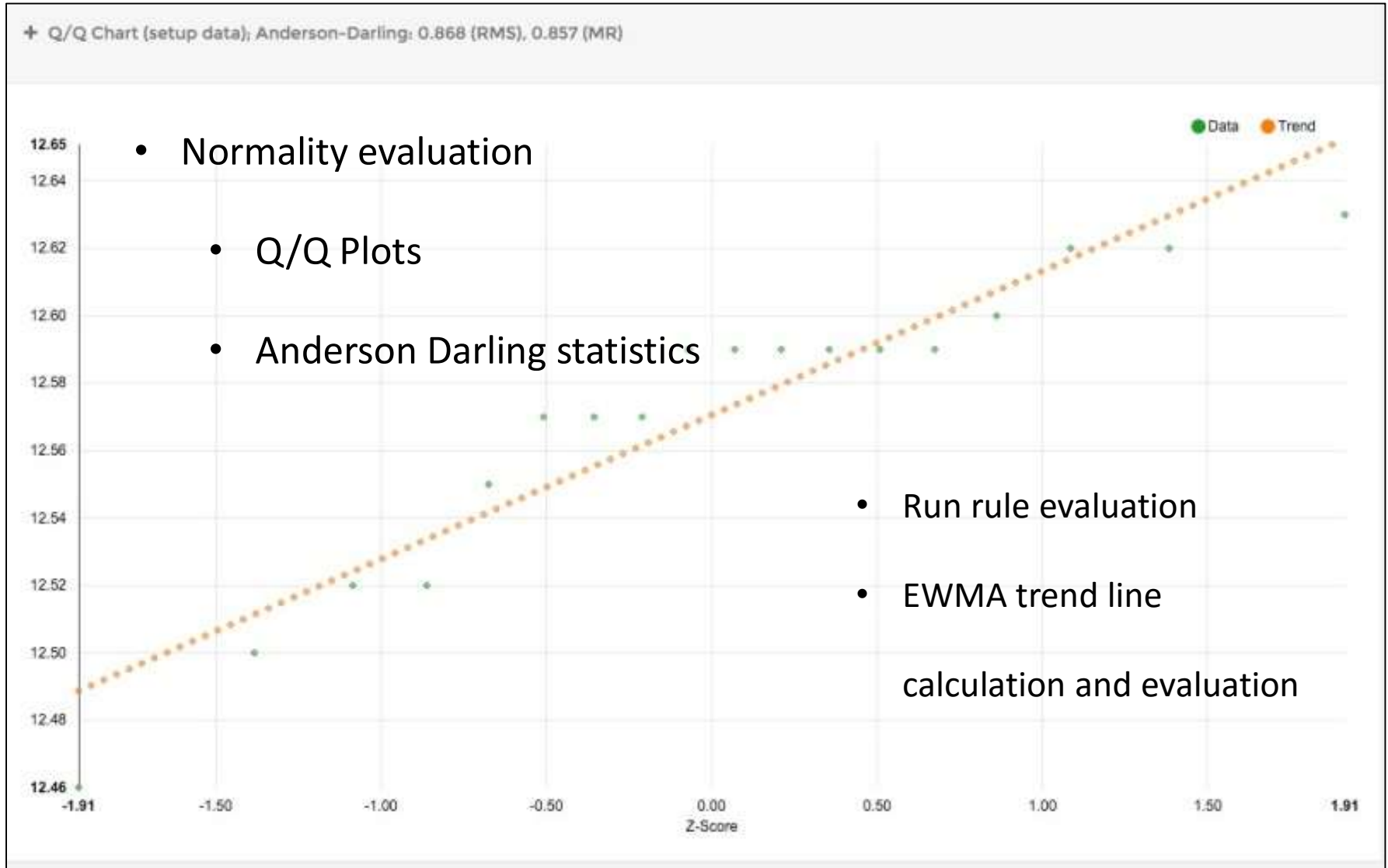


ASTM D6299 and 40 CFR 80.47 - continued

- Moving range charts
- Outlier evaluation



ASTM D6299 and 40 CFR 80.47 - continued



ASTM D6299 and GPA 2198

- GPA 2198 speaks to the same types of control charting practices as D6299, although with less specificity. Example
 - I charting is explicit in D6299, implied in GPA 2198
- Other aspects of ASTM D6299 control charting that are not addressed in GPA 2198:
 - Normality assessment
 - Moving range chart preparation
 - Pre-treatment of results
 - F-test for similar variances and t-test for means
 - Methods for identifying outliers
 - Calculation of trend
 - Transition to next QC material (e.g., Q-procedure)
 - ASTM allows use of EWMA run rules

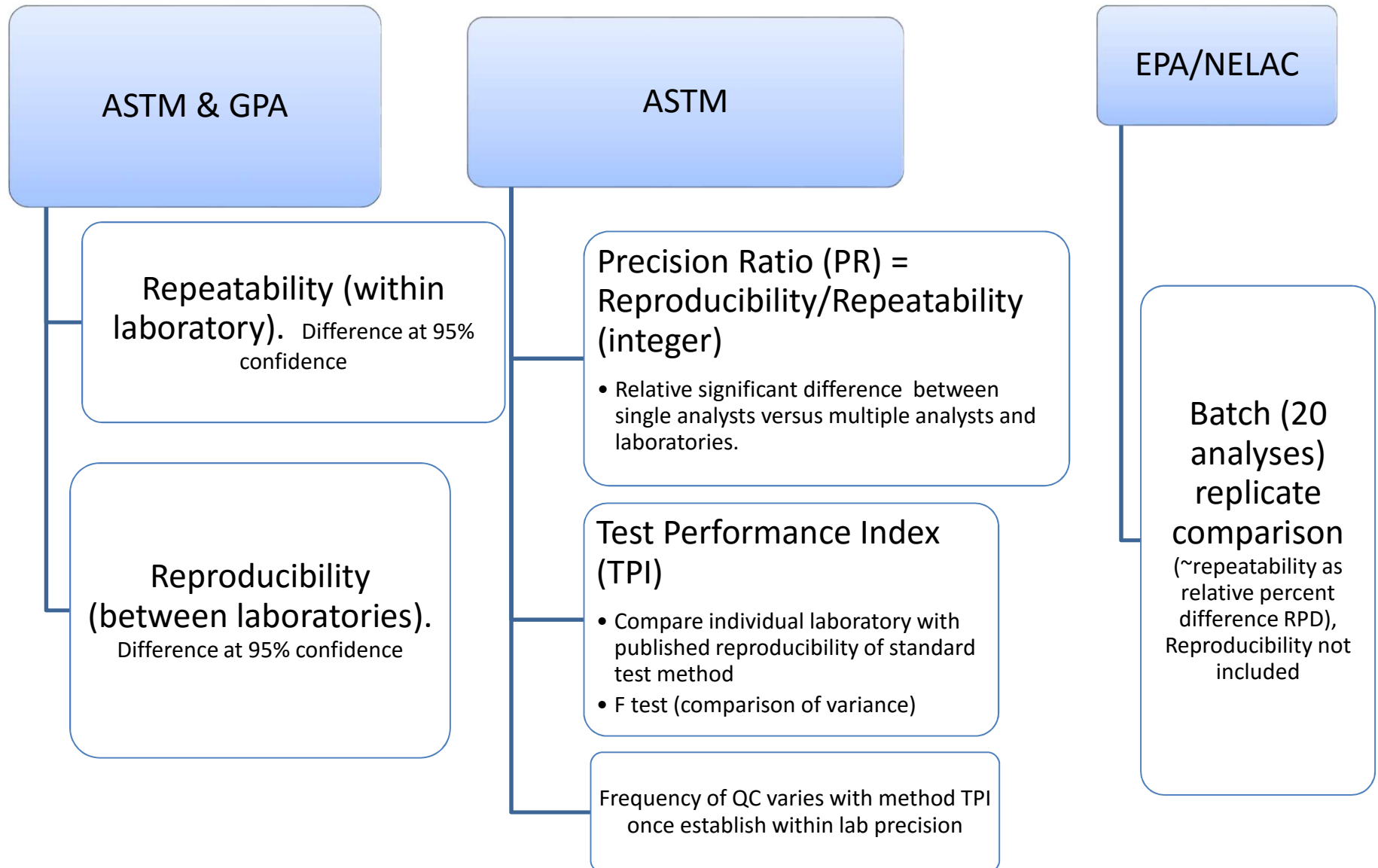
Cross Program Practices

	EPA	GPA	ASTM
Calibration	Initial and ongoing with method defined criteria	Calibration plots for "linearity", Fidelity plots	Test method specific. Initial/on-going typical
Negative Control	Field, laboratory blanks compared sensitivity limits	Not discussed	Blanks in some methods
Accuracy Control (calibration)	Calibration verification check standard	Nothing equivalent for bias	Check Standard
Accuracy Control (surrogate/IS)	Surrogates, internal standards	Nothing equivalent	Internal standards in some methods
Accuracy Control (matrix spike)	Matrix spike	Nothing equivalent	Nothing equivalent
Accuracy Control (PT)	PT	Control charts	Control charts, SQC of reference material, inter-laboratory cross check










Cross Program Practices

	EPA	GPA	ASTM
Precision Control (samples)	Batch duplicates (samples, spikes), RPD criteria in methods or lab derived	Daily sample duplicates, repeatability criteria in methods	SQC of samples, repeatability and reproducibility criteria in methods
Precision Control (standards)	Nothing equivalent	Daily calibration standard duplicate, reproducibility criteria in methods	SQC of reference material, repeatability and reproducibility criteria in methods

Precision Comparison



Hydrocarbon Testing Unification

	ASTM	GPA	Tier III (EPA)
Embedded QC Practices -control charting -check standards - positive & negative controls -internal standards -surrogates	 Surrogates NA	Not included: <ul style="list-style-type: none"> • Internal Standards • negative controls • Surrogates 	
Reference to a specific petroleum lab quality system practices		None	None within EPA methods
Specific/strict initial calibration requirements		None	
Interlaboratory accuracy/precision checks			None
PT/SRM Program			Within some programs

Thank You



ENVIRONMENTAL[®]
STANDARDS

“Setting the Standards for Innovative Environmental Solutions”

Headquarters 1140 Valley Forge Road | PO Box 810 | Valley Forge, PA 19482 | 610.935.5577

Virginia 1412 Sachem Place, Suite 100 | Charlottesville, VA 22901 | 434.293.4039

Tennessee 8331 East Walker Springs Lane, Suite 402 | Knoxville, TN 37923 | 865.376.7590

New Mexico PO Box 29432 | Santa Fe, NM 87592 | 505.660.8521

Illinois PO Box 335 | Geneva, IL 60134 | 630.262.3979

Web www.envstd.com | **E-mail** solutions@envstd.com